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AUTHOR(S):

Nakagawa, Hiroyuki; Yamaguchi, Emi

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Influence of oxalic acid formed on the degradation of phenol by Fenton reagent

Hiroyuki Nakagawa* and Emi Yamaguchi

Environment Preservation Research Center, Kyoto University, Yoshida-Honmachi,

Sakyo-ku, Kyoto 606-8501, JAPAN

* Corresponding author. Tel.: +81 75 753 7715; fax +81 75 753 7710.

E-mail address: hiroyuki@cheme.kyoto-u.ac.jp (H. Nakagawa).

19 ABSTRACT

20 The objective of this work is to examine the influence of oxalic acid formed
21 on the degradation of phenol by Fenton reagent. Oxalic acid formed at initial stage
22 within 30 min significantly suppresses the reduction of ferric ion, thus terminating
23 degradation reaction. The yield of oxalic acid is dependent on the amount of ferrous
24 ion dosed since the minimal amount of oxalic acid is formed after the degradation
25 reaction terminates. Mineralization of phenol by Fenton reagent stagnates after 120
26 min under the conditions used in this study. The reason why the mineralization
27 stagnated can be assumed to be following two mechanisms other than the depletion of
28 H₂O₂. In the case where a small amount of ferrous ions is dosed, the reduction of ferric
29 ions is minimal by oxalic acid formed. In the case where a large amount of ferrous ions
30 is dosed, the amount of degradable organic compounds is insufficient owing to
31 preferential conversion to oxalic acid. The mineralization can be enhanced by the
32 intermittent dosing of ferrous ions, which facilitates the suppression of oxalic acid
33 formation during the degradation by Fenton reagent.

34
35 KEY WORD: Fenton reaction, Phenol degradation, Mineralization, Oxalic acid

1. Introduction

Treatment of wastewater containing organic pollutants has been of great concern all over the world. Advanced oxidation processes (AOPs) have great potential in treating wastewater containing organic pollutants at room temperature, and a number of AOPs have been proposed. Among them, Fenton oxidation, in which wastewater is treated with Fenton reagent (ferrous salt + H₂O₂), is an attractive oxidative process for wastewater treatment because iron is a very abundant and non-toxic element and hydrogen peroxide is easy to handle and environmentally safe (Andreozzi et al., 1999). Therefore, it has been adopted as the process for treating various industrial wastes (Wadley and Waite, 2004; Bautista et al., 2008).

In Fenton oxidation, a very active hydroxyl radical formed during reactions involving Fenton reagent (Reaction (1)) attacks organic compounds, enabling these compounds to be degraded through oxidation (Harber and Weiss, 1934).



The regeneration of Fe(III) to Fe(II) through the reduction by H₂O₂ or HO₂· formed from H₂O₂ also occurs in this reaction system (Barb et al., 1951a, 1951b; Walling, 1975). Therefore, as long as H₂O₂ is available, the redox cycle of iron ions is basically continuous between Fe(II) and Fe(III), thus forming a hydroxyl radical. It is essential to

promote this cycle in order to degrade organic compounds efficiently. It is well known that with the Fenton process, this mineralization is very likely to stagnate before it is complete. Therefore, the Fenton process has been proposed primarily as a pretreatment to reduce the effluent toxicity to safe levels and to improve biodegradability for further biological treatment (Chamarro et al., 2001; Lopez et al., 2004). In order to enhance the degree of mineralization and thus the usefulness of the Fenton process, it is necessary to analyze the intermediate products that remain in the water treated with Fenton reagent and to examine the reasons why the mineralization stagnates.

It has been noted that the benzenediols and benzoquinones could expedite the redox cycle of iron (Tamagaki et al., 1989a, 1989b; Chen and Pignatello, 1997). Mijangos et al. (2006) examined the changes in solution color during treatment and reported that the observed color was due to an intermediate product of the main reaction, such as benzoquinones or benzene rings coordinated with ferric ions. Kang et al. (2002) focused on the interaction of the organic intermediates with the Fe species. Zimbron and Reardon (2009) suggested that organic intermediates formed during pentachlorophenol degradation by Fenton reagent have a HO· scavenging effect from the kinetic model calculation. Among these intermediate products, we focus on the relatively stable organic acids, which may remain after the treatment, in order to enhance the degree of

mineralization. Acetic, maleic, malonic, and oxalic acids are known to be poorly degradable by Fenton reagent (Bigda, 1995). In particular, oxalic acid can deactivate Fe ion activity by the strong coordination with Fe(III) (Sun and Pignatello, 1992, 1993; Kwon et al., 1999). Zazo et al. (2005) reported that oxalic acid reached a high relative concentration among organic acids formed during phenol degradation by Fenton reagent, although its formation rate was lower than that of other acids. They also reported that the concentration of oxalic acid increased at increasing ferrous ion dose (Zazo et al., 2007).

In this study, we focus on the formation of organic acids, especially oxalic acid, and discuss its influence on the degradation of phenol by Fenton reagent. We examine the effect of the reaction conditions on the formation behavior of oxalic acid. We discuss the influence of oxalic acid on the consumption of H_2O_2 and the mineralization behavior under the conditions used in this study for the view point of iron cycle. Finally, we propose a method for enhancing the degree of mineralization using the same amount of Fenton reagent.

2. Experimental methods

2.1. Chemicals

All chemicals were purchased from WAKO Pure Chemical Industries. Phenol (> 99%) was used as the organic pollutant in this study. It was used without any other purification. A 1000 mg L⁻¹ phenol solution was prepared using distilled water and was stored in a glass bottle. Solutions of FeSO₄·6H₂O and Fe₂(SO₄)₃·9H₂O (0.25 M each) were prepared and used as ferrous and ferric ion sources, respectively.

2.2. Procedure

The reactor was a 300 mL glass beaker with a magnetic stirrer. We prepared 250 mL of a 100 mg L⁻¹ phenol solution, adjusted the pH to 3.0 using 0.1 M H₂SO₄, and dosed a designated amount of H₂O₂ solution (15 wt%). We then dosed a designated amount of 0.25 M FeSO₄ to initiate the reaction. The experiment was carried out at room temperature (23 ± 2 °C) in a dark room to avoid the effect of light. The initial concentrations of ferrous ion, C_{Fe(II),0}, and H₂O₂, C_{H2O2,0}, in a reactor were varied from 0.1 to 1.5 mM and from 5 to 80 mM, respectively.

2.3. Analysis

The treated water was analyzed immediately after the treatment. The concentrations of phenol and H₂O₂ were determined by colorimetric methods with a UV-Vis spectrometer (UVmini-1240, Shimadzu). The 4-aminoantipyrine and iodide methods (Allen et al., 1952; Kormann et al., 1988) were utilized for the analysis of

phenol and H_2O_2 at $\lambda = 507$ and 350 nm, respectively. The total organic carbon (TOC) concentration was measured using a TOC analyzer (TOC-V_{CSH}, Shimadzu). The quantitative measurement of organic acids was carried out by using a non-suppressor-type ion chromatograph system equipped with a Shim-pack IC-A1 column (100 mm long). An aqueous solution of phthalic acid (2.5 mM) and tris(hydroxymethyl)aminomethane (2.4 mM) was used as the mobile phase at a flow rate of 1.5 mL min^{-1} under isocratic conditions. Prior to analysis, treatment using a solid-phase extraction cartridge was performed in order to remove ferric ions from organic acid because ferric ions interfere with the quantitative analysis of oxalic acids, as is examined in Supplementary Material (SM).

3. Results and discussion

3.1. Mineralization behavior of phenol during the degradation by Fenton reagent

Phenol was degraded by more than 95% within a few minutes under the conditions performed in this study. Therefore, the TOC concentration, which is directly correlated to the degree of mineralization, is examined. Figure 1 shows the change of the TOC yield, Y_{TOC} , against treatment time when $C_{\text{Fe(II),0}}$ or $C_{\text{H}_2\text{O}_2,0}$ was varied. $C_{\text{Fe(II),0}}$ and $C_{\text{H}_2\text{O}_2,0}$ were 1.0 and 20 mM, respectively. Under the reaction conditions examined,

the Y_{TOC} significantly decreased just after the reaction was initiated, and then decreased more gradually. Mineralization appeared to stagnate after 120 min in all cases. $C_{\text{Fe(II)},0}$ affects the mineralization rate in the initial stage, however, it has little effect on the mineralization rate after 120 min. About 60% of the carbon contained in the phenol remained in the water at 240 min. $C_{\text{H}_2\text{O}_2,0}$ had a similar effect on the mineralization behavior of phenol as $C_{\text{Fe(II)},0}$ although the effect was more significant.

Next, the consumption of H_2O_2 during the treatment is examined. Figure 2 shows the change of the concentration of H_2O_2 , $C_{\text{H}_2\text{O}_2}$, as a function of time at various values of $C_{\text{Fe(II)},0}$ and at $C_{\text{H}_2\text{O}_2,0} = 20$ mM. H_2O_2 was rapidly consumed in the initial stage within 30 min. This rapid consumption indicated that severe degradation occurred and terminated within 30 min. After 30 min, minimal H_2O_2 was consumed when $C_{\text{Fe(II)},0}$ was less than 0.5 mM. On the other hand, $C_{\text{H}_2\text{O}_2}$ gradually decreased when $C_{\text{Fe(II)},0}$ was 1.0 mM. $C_{\text{H}_2\text{O}_2}$ values at 240 min were 0.2, 6.6, and 10.4 mM in the case of 1.0, 0.5, and 0.25 mM of $C_{\text{Fe(II)},0}$, respectively, whereas a significant difference was not observed in Y_{TOC} values among the three cases. Stagnation of the mineralization after 120 min in the case of $C_{\text{Fe(II)},0} \leq 0.5$ mM was not due to the depletion of H_2O_2 because sufficient H_2O_2 remained in the treated water. Therefore, the organic products, which are supposed to be organic acids, were analyzed to examine the influence of organic acids on the

degradation by Fenton reagent.

3.2. Formation behavior of oxalic acid

Oxalic acid and formic acid could be quantified in the treated water in this study. Other organic acids such as acetic acid, glycolic acid, malonic acid, malic acid, and tartaric acid were also detected in the case of low $C_{\text{Fe(II)},0}$, however, their yields, which were all less than $0.025 \text{ g-C g-C}^{-1}$, were too low to be quantified. Figure 3 shows the yields of oxalic acid (Y_{oxalic}), formic acid (Y_{formic}), Y_{TOC} , and $C_{\text{H}_2\text{O}_2}$ as a function of $C_{\text{Fe(II)},0}$ value in the degradation of phenol by Fenton reagent for 150 min. The yield of organic acid was represented on a carbon basis, so that it could be compared with Y_{TOC} directly. Y_{oxalic} was significantly dependent on $C_{\text{Fe(II)},0}$. At $0.12 \text{ g-C g-C}^{-1}$, the Y_{oxalic} corresponded to just 16% of the carbon remaining in the treated water when phenol was treated with 0.1 mM of $C_{\text{Fe(II)},0}$. It increased with the increase of $C_{\text{Fe(II)},0}$, and reached as high as $0.55 \text{ g-C g-C}^{-1}$ when phenol was treated with 1.5 mM of $C_{\text{Fe(II)},0}$. The ratio of Y_{oxalic} to Y_{TOC} exceeded 0.8, indicating that carbon remaining in the treated water almost existed as oxalic acid. It can be said that oxalic acid was preferentially formed at high $C_{\text{Fe(II)},0}$ because Y_{TOC} of the degradation with 1.5 mM of $C_{\text{Fe(II)},0}$ was almost the same as that of the degradation with 0.3 mM of $C_{\text{Fe(II)},0}$ at 150 min. The formation of formic acid

was insignificant compared with oxalic acid and could not be quantified in the case of

$C_{\text{Fe(II)},0} \geq 1.0 \text{ mM}$.

As for the formation profile of oxalic acid, a significant amount of oxalic acid was formed at the initial stage within 30 min and its yield appeared to be almost unchanged after 60 min under various values of $C_{\text{Fe(II)},0}$ and $C_{\text{H}_2\text{O}_2,0}$ (Fig. SM-1). These results related to the formation behavior of oxalic acid are consistent with the report of Zazo et al. (2007). Since the oxalic acid is not degraded by Fenton reagent solely, degradation proceeded slowly to decrease TOC concentration after 60 min, as shown in Fig. 1. 89% of the carbon contained in the phenol was converted to CO_2 or oxalic acid at 150 min in the case of $C_{\text{Fe(II)},0} = 1.0 \text{ mM}$. It can be said that the degradation of organic compounds in the treated water almost went to completion in the case of $C_{\text{Fe(II)},0} = 1.0 \text{ mM}$ because oxalic acid is the final product of the degradation by Fenton reagent as well as CO_2 . On the other hand, the degradation seemed not to go to completion in the case of $C_{\text{Fe(II)},0} = 0.2 \text{ mM}$ because the sum of the yields of oxalic acid and CO_2 is $0.47 \text{ g-C g-C}^{-1}$ at 150 min.

3.3. Effect of oxalic acid on the iron cycle in the water

Degradation mainly proceeds by the formation of an active radical through the iron cycle between Fe(II) and Fe(III) . The rate of the iron cycle is determined by the

reduction rate of Fe(III) because the oxidation rate of Fe(II), Reaction (1), is very rapid.

Therefore, the reducing behavior of Fe(III) is examined here.

Considering that enough H_2O_2 remains at 150 min as shown in Fig. 2, it is possible that the degradation rate is extremely slow; therefore, prolonged treatment is required for oxalic acid formation when $C_{\text{Fe(II)},0}$ is low. Thus, the degradation was performed for 24 h at various values of $C_{\text{Fe(II)},0}$ and at $C_{\text{H}_2\text{O}_2,0} = 20$ mM. Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ at 24 h are shown in Fig. 4.. H_2O_2 was additionally dosed to be 20 mM at 240 min only in the case of $C_{\text{Fe(II)},0} = 1.0$ mM because H_2O_2 was almost consumed. Y_{oxalic} in the cases of $C_{\text{Fe(II)},0} = 0.2$ and 0.5 mM showed minimal increase by extending the treatment time, and it was much lower than that for $C_{\text{Fe(II)},0} = 1.0$ mM at 150 min, although a considerable amount of H_2O_2 remained in the treated water. These results clearly show that oxalic acid cannot be produced in the case of low $C_{\text{Fe(II)},0}$ as much as it can in the case of high $C_{\text{Fe(II)},0}$. Therefore, it is considered that Fe(III) is minimally reduced, in other word, the activity of Fe(III) is significantly lowered, during the degradation. It has been reported that the strong coordination of oxalic acids to ferric ions deactivates the degradation activity of ferric ions, as stated in the introduction. There is another possibility that the unidentified products are difficult to degrade by Fenton reagent, although Zazo et al. (2007) reported that they were the precursors of oxalic acid.

199 To examine the deactivation effects of oxalic acid under the conditions
200 performed here, two experiments were employed. One was the addition of ferric ions to
201 the water treated with 0.2 mM of $C_{\text{Fe(II)},0}$ and the other was the comparison of H_2O_2
202 consumption rates in the water containing oxalic acid. In the former experiment, ferric
203 ion was additionally dosed in the water treated with 0.2 mM of $C_{\text{Fe(II)},0}$ for 24 h so that
204 the concentration of total iron ions was 1.0 mM. Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ were measured
205 60 min after additional dosing at 24 h, and the results are shown in Fig. 4. Y_{TOC}
206 decreased significantly from 0.53 to 0.45 g-C g-C⁻¹ and Y_{oxalic} reached 0.32 g-C g-C⁻¹.
207 Degradation was found to proceed significantly by the addition of ferric irons. This
208 result clearly indicates that the remaining organic compounds were degradable by
209 Fenton reagent and that the stagnation of the mineralization was due to the deactivation
210 of Fe(III). It was also confirmed that some of the unidentified products were the
211 precursors of oxalic acid. As for the comparison of H_2O_2 consumption rate, Fig. 5
212 compares the change of $C_{\text{H}_2\text{O}_2}$ as a function of time in the water containing 1.0 mM of
213 $C_{\text{Fe(III)}}$ with various concentrations of oxalic acid, C_{oxalic} . 80% of H_2O_2 was consumed in
214 120 min when no oxalic acid was present in the water. In the case of $C_{\text{oxalic}} = 0.5$ mM,
215 H_2O_2 was consumed as is the case with no oxalic acid whereas only 25% of H_2O_2 was
216 consumed in the case of $C_{\text{oxalic}} = 1$ mM. When C_{oxalic} was 1.5 mM, minimal H_2O_2 was

consumed. Thus, the activity of Fe(III) is almost lost if the molar ratio of C_{oxalic} to $C_{\text{Fe(III)}}$ exceed 1.5 in the absence of reducing agent.

The consumption behavior of H_2O_2 shown in Fig. 2 is examined here. H_2O_2 was more rapidly consumed in the initial stage within 30 min compared with the case in which there was no oxalic acid, as shown in Fig. 5. This is because the reduction of Fe(III) occurred not only by H_2O_2 but also by the degradation products. In this initial stage, a considerable amount of oxalic acid is produced to deactivate Fe(III). The consumption rate of H_2O_2 was significantly reduced after 30 min in the case of $C_{\text{Fe(II)},0} \leq 0.5$ mM because the molar ratio of C_{oxalic} to $C_{\text{Fe(III)}}$ had already exceeded 2. Therefore, the yield of oxalic acid is dependent on the $C_{\text{Fe(II)},0}$. On the other hand, in the case of $C_{\text{Fe(II)},0} = 1.0$ mM, H_2O_2 was gradually consumed. Organic intermediates in the water may act as reducing agents for Fe(III), because the molar ratio of C_{oxalic} to $C_{\text{Fe(III)}}$ was 1.5. Stagnation of mineralization was observed after 120 min in both cases, as shown in Fig. 1, but the situation was different in those cases. In the former case, Fe(III) was minimally reduced by the coordination of oxalic acid although a fairly large amount of H_2O_2 and degradable organic compounds remained in the water. In the latter case, the amount of degradable organic compounds is insufficient because of preferential conversion to oxalic acid, although reduction of Fe(III) occurred slowly.

3.4. Enhancement of the mineralization degree using same amount of Fenton reagent

It is, of course, desirable to enhance the degree of mineralization, in other words, to reduce Y_{TOC} . Figure 4 helps us to examine the conditions that reduce Y_{TOC} . At 24 h, the degradation with 0.5 mM of $C_{\text{Fe(II)},0}$ gave lower Y_{TOC} compared to that with 1.0 mM of $C_{\text{Fe(II)},0}$. In the case of $C_{\text{Fe(II)},0} = 1.0$ mM, Y_{TOC} was reduced only slightly with the prolonged treatment because a large part of organic compounds is oxalic acid even at 150 min. As a result, 97% of the remaining carbon was oxalic acid at 24 h because $Y_{\text{oxalic}}/Y_{\text{TOC}} = 0.97$. On the other hand, the organic compounds that can be mineralized remained in the degradation with 0.5 mM of $C_{\text{Fe(II)},0}$ at 150 min. Therefore, Y_{TOC} could be reduced from 0.63 to 0.47 g-C g-C⁻¹ by prolonged treatment, although the mineralization rate was very slow. From these results, Y_{TOC} can be reduced if the degradation is allowed to proceed with a lower concentration of oxalic acid. To achieve this situation, ferrous ion was supplied in intermittent doses. The same amount of ferrous ion was dosed every 120 min a total of four times so that the total concentration of iron ions was 1.0 mM. $C_{\text{H}_2\text{O}_2,0}$ was 40 mM. Figure 6 shows the Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ at 480 min. Four intermittent doses were effective in enhancing the degree of mineralization. Y_{TOC} in the case of four intermittent dosing was significantly reduced to 0.39 g-C g-C⁻¹, whereas that in the case of all-at-once dosing was 0.53 g-C g-C⁻¹,

although the consumption of H_2O_2 was almost the same in both cases. The formation of oxalic acid was also suppressed by four intermittent dosing as expected. Phenol was eventually converted to CO_2 or oxalic acid through the unidentified products during the degradation by Fenton reagent. It was found that intermittent dosing was effective for converting the unidentified products to CO_2 preferentially. Thus, the mineralization degree could be enhanced by employing intermittent dosing using same amount of Fenton reagent.

4. Conclusions

In this study, the influence of oxalic acid on the degradation of phenol by Fenton reagent was examined. Oxalic acid formed during the degradation was found to suppress the reduction of ferric ions by coordination, terminating the degradation reaction in the initial stage within 30 min. Since the minimal amount of oxalic acid was formed after the degradation reaction terminated, the yield of oxalic acid was dependent on the amount of ferrous ion dosed. Mineralization of phenol by Fenton reagent stagnated after 120 min under the conditions used in this study. The reason why the mineralization stagnated was assumed as follows: In the case where a small amount of ferrous ions was dosed, the reduction of ferric ions was minimal by oxalic acid formed,

although a fairly large amount of H_2O_2 and degradable organic compounds remained in the water. The fact that the degradation proceeded significantly by dosing additional ferric ions to the treated water supports this result. In the case where a large amount of ferrous ions was dosed, the amount of degradable organic compounds was insufficient owing to preferential conversion to oxalic acid, although H_2O_2 was gradually consumed.

Phenol was eventually converted to CO_2 or oxalic acid through the unidentified products during the degradation by Fenton reagent. Therefore, it was inferred that TOC can be reduced significantly if the degradation is allowed to proceed with a lower concentration of oxalic acid. A same amount of ferrous ion was supplied in four intermittent doses for this purpose. TOC yield could be reduced by 26% compared to the degradation with all-at-once dose when the same amounts of ferrous ion and H_2O_2 were used. The yield of oxalic acid was also suppressed by intermittent dosing as expected. These results indicated that intermittent dosing of ferrous ion was effective for converting phenol to CO_2 rather than oxalic acid through the unidentified degradation products.

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Figure Captions

Fig. 1. The change of the TOC concentration against treatment time during the degradation of phenol by Fenton reagent when (a) $C_{\text{Fe(II)},0}$ was varied. (b) $C_{\text{H}_2\text{O}_2}$ was varied.

Fig. 2. The change of the concentration of H_2O_2 as a function of time during the degradation of phenol by Fenton reagent when $C_{\text{Fe(II)},0}$ was varied.

Fig. 3. The yields of oxalic acid, formic acid, Y_{TOC} , and $C_{\text{H}_2\text{O}_2}$ as a function of $C_{\text{Fe(II)},0}$ value during the degradation of phenol by Fenton reagent for 150 min.

Fig. 4. Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ in the prolonged degradation when $C_{\text{Fe(II)},0}$ was 0.2, 0.5, and 1.0 mM.

Fig. 5. Comparison of the change of $C_{\text{H}_2\text{O}_2}$ as a function of time in the water containing 1.0 mM of $C_{\text{Fe(III)}}$ with various concentrations of oxalic acid.

Fig. 6. Comparison of the Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ at 480 min between four intermittent doses and all-at-once dose of Fe^{2+} when the same amounts of Fe^{2+} and H_2O_2 were dosed.

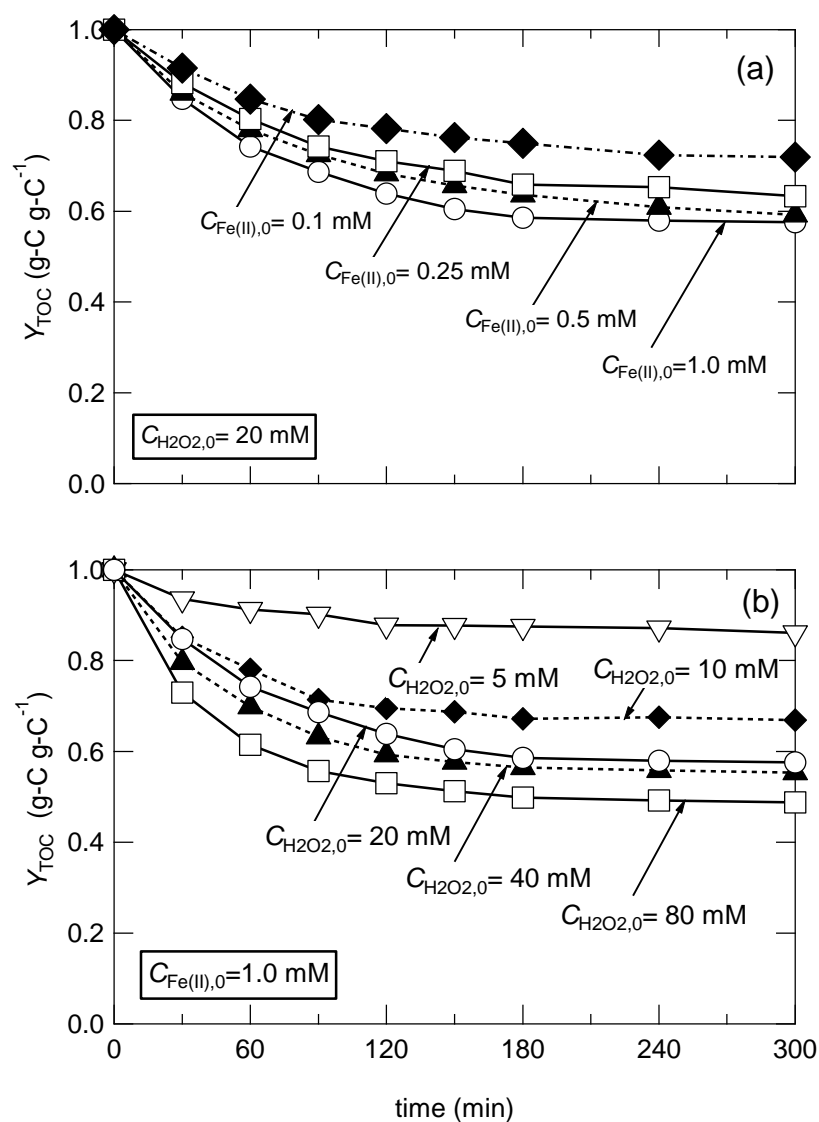


Fig. 1 The change of the TOC concentration against treatment time during the degradation of phenol by Fenton reagent when (a) $C_{Fe(II),0}$ was varied. (b) $C_{H_2O_2}$ was varied.

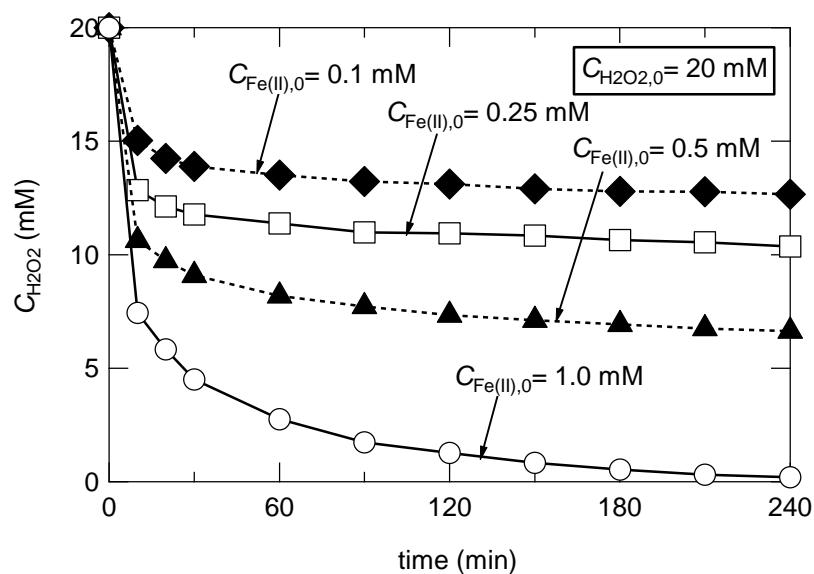


Fig. 2 The change of the concentration of H_2O_2 as a function of time during the degradation of phenol by Fenton reagent when $C_{\text{Fe(II)},0}$ was varied.

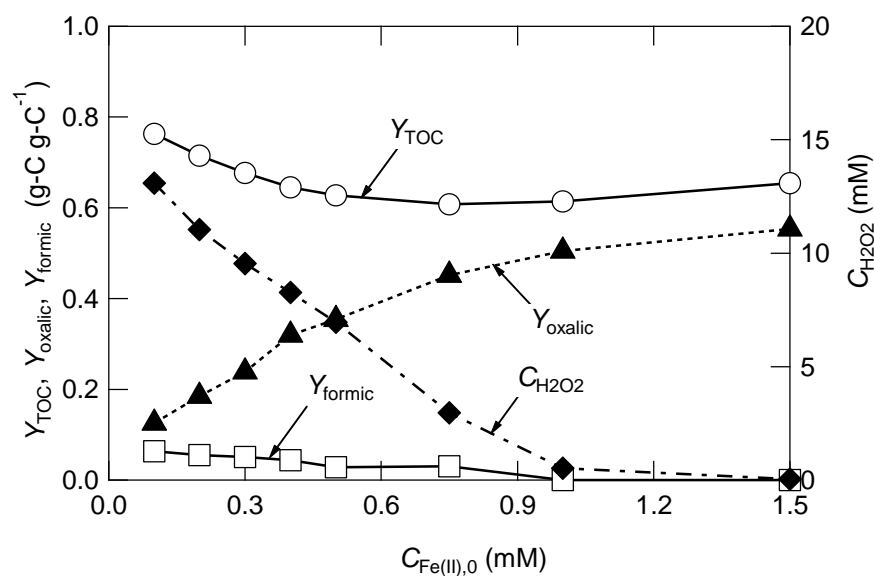
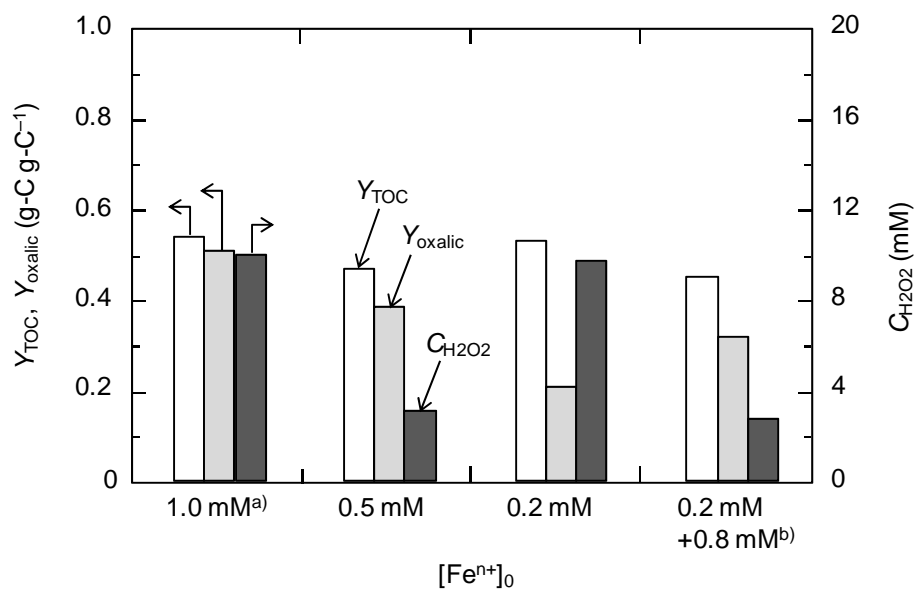


Fig. 3 The yields of oxalic acid, formic acid, Y_{TOC} , and $C_{H_2O_2}$ as a function of $C_{Fe(II),0}$ value during the degradation of phenol by Fenton reagent for 150 min.



a) H_2O_2 was additionally dosed at 240 min to be 20 mM because H_2O_2 was almost consumed.

b) Fe^{3+} was dosed to the water treated with 0.2 mM of $C_{\text{Fe(II)},0}$ at 24 h so that the total amount of iron ions dosed was same as that of treated with 1.0 mM of $C_{\text{Fe(II)},0}$.

Fig. 4 Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ in the prolonged degradation when $C_{\text{Fe(II)},0}$ was 0.2, 0.5, and 1.0 mM.

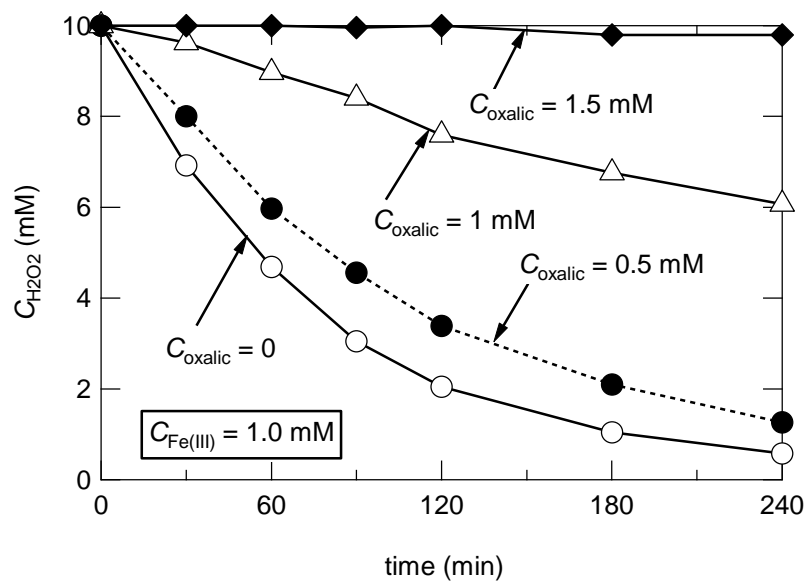


Fig. 5 Comparison of the change of $C_{\text{H}_2\text{O}_2}$ as a function of time in the water containing 1.0 mM of $C_{\text{Fe(III)}}$ with various concentrations of oxalic acid.

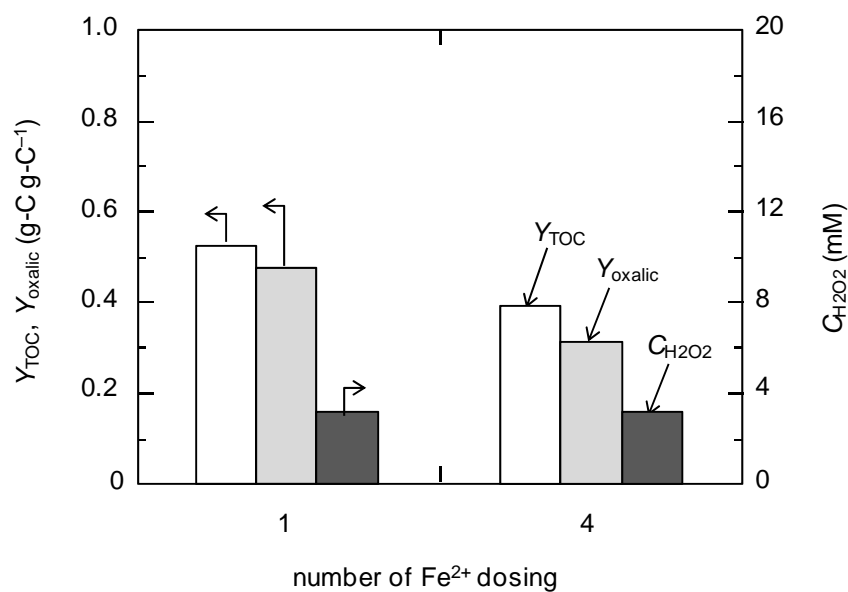


Fig. 6 Comparison of the Y_{TOC} , Y_{oxalic} , and $C_{H_2O_2}$ at 480 min between four intermittent doses and all-at-once dose of Fe^{2+} when the same amounts of Fe^{2+} and H_2O_2 were dosed.